

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
13 June 2002 (13.06.2002)

PCT

(10) International Publication Number  
**WO 02/46323 A2**

- (51) International Patent Classification<sup>7</sup>: **C09D 11/00**
- (21) International Application Number: PCT/IL01/01116
- (22) International Filing Date: 4 December 2001 (04.12.2001)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:  
60/251,385 6 December 2000 (06.12.2000) US
- (71) Applicant (*for all designated States except US*):  
**PRINTAR LTD.** [IL/IL]; 5 Oppenheimer St., 76000 Rehovot (IL).
- (72) Inventors; and
- (75) Inventors/Applicants (*for US only*): **ZOHAR, Ron** [IL/IL]; 12 Savyon St., 70800 Gan Yavne (IL). **MOZEL, Jacob** [IL/IL]; 11 Hakalanit St., 44280 Kfar Saba (IL). **SAMUEL, Joshua** [IL/IL]; 7 Rabi Tarfon St., 93592 Jerusalem (IL).
- (74) Agent: **NOAM, Meir**; P.O. Box 34335, 91342 Jerusalem (IL).
- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:  
— without international search report and to be republished upon receipt of that report
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*



**WO 02/46323 A2**

(54) Title: UV CURABLE INK-JET LEGEND INK FOR PRINTING ON PRINTED CIRCUIT BOARDS

(57) Abstract: An ultraviolet curable composition for printing on a printed circuit board using an inkjet printer comprising a mixture of reactive monomers and oligomers, at least one pigment, at least one photoinitiator, and at least one additive. The monomer/oligomer mixture is formulated so that the ink has a high viscosity of about 40-200 cp at 25 °C, and a low viscosity of about 10-20cp at a high temperatures of about 50-80 °C. The cured image is able to withstand dipping in a solder bath at 260 °C without substantial degradation.

## UV CURABLE INK-JET LEGEND INK FOR PRINTING ON PRINTED CIRCUIT BOARDS

### FIELD OF THE INVENTION

The present invention relates to the field of printed circuit boards (PCB's). More specifically, the present invention relates to a UV curable legend ink for printing on PCB's using an ink jet printer.

### BACKGROUND OF THE INVENTION

Printed circuit boards serve to interface and connect the various components in electronic devices. The production of a PCB is a multi-step process that includes marking the PCB with a legend showing the location of each part on the board, the identification number, and the polarity of the part. Other markings may also be necessary.

Typically, the PCB legend is formed through screen-printing, using a screen stencil and a curable (heat, UV, or EB) ink that is pressed through the stencil. Screen-printing requires making a new stencil for printing every type of printed board. Therefore, in the case of printed boards produced in a small lot, the printing cost per printed circuit board is greatly increased. Screen-printing has other disadvantages such as the minimal achievable pitch i.e. inability to produce legible characters of small dimensions (e.g. 0.5mm characters).

Ink jet printing provides an ideal solution to the aforementioned problems. Ink jet printing is a process whereby an image is printed directly from an electronic file onto a substrate, without contact between the printing device and the substrate. Printing occurs via projection of a stream of ink droplets to a surface while controlling the direction of the stream so that the droplets are caused to form the desired printed image on the surface. An ink jet printer for use in printing legends on printed circuit boards is described in PCT/IL01/00596, entitled, "Jet Print Apparatus and Method for Printed Circuit Board Manufacture". Ink jet printing of PCB's provides the following advantages: (1) there is no need to produce a stencil for each type of PCB; (2) direct digital printing enables digital compensation and correction of distortion of the PCB; (3) the demanding step of placing the screen over the PCB (in screen printing) is avoided; (4) small characters, not legible using screen printing, may be printed by

the precise drop placement of ink jet printing.

Commercial legend inks for PCB's are typically viscous pastes which are comprised of curable polymers, oligomers, monomers, and solid particulate fillers with particle size of about 5 microns. These inks are not appropriate for use in an ink jet printer. An ink jet ink needs to have an appropriate viscosity and surface tension in order to enable jetting. The ink must have a particle size small enough so as to enable passage through the ink jet nozzle without clogging. Also, the printed legend must be able to withstand immersion in a solder bath of about 250 deg. C without yellowing. In general, the legend must conform to the standards set out in IPC-TM-650 test methods (the Institute for Interconnecting and Packaging Electronic Circuits) and to legibility guidelines set out in IPC-A600.

Conventional ink jet inks form a solid layer on the substrate after printing, by evaporation of the solvent in which the pigment is dispersed, or by using a phase change ink, or by UV curing while using suitable monomers and oligomers. However, conventional ink jet inks, which are designed for graphic arts or even for textile, are not suitable for printing onto PCB surfaces, due to the very extreme conditions which the printed pattern is exposed to, such as very high temperatures in the solder bath, or presence of very aggressive solvents, which could dissolve the printed pattern, or could decrease the adhesion of the printed legend to the PCB.

U.S. Patent No. 5,270,368 discloses a UV curable ink composition for printing an etch resist pattern on a copper clad board. The ink is comprised of at least 8% of an acrylate containing a pendant carboxylic group to enable stripping by a basic solution. This makes the ink unsuitable for legend printing, as the legend is permanent and therefore needs to be impervious to various forms of chemical attack. Furthermore, the low viscosity at 25°C (1-10 cp) hastens the settling of the ink pigments, thus appreciably shortening the shelf life of the ink.

Typical UV curable inks, such as the type disclosed in U.S. Pat. No. 6,114,406, describing a radiation curable ink composition, have a pigment loading of up to 10%. Higher pigment loading tends to interfere with curing of the films because of light scattering and absorption. However, the relatively low pigment loading typical of inks used in graphic arts, particularly in the case of white pigments, does not yield a sufficiently opaque printing that is acceptable for printing the legend on the PCB. An additional drawback of commonly available UV curable ink jet inks is that they

are not designed to withstand the high temperatures (up to 260°C) which the ink must be able to withstand for limited periods of time.

It is therefore the object of the present invention to provide a UV ink for ink jet printing onto PCB's that overcomes the aforementioned problems including those associated with the extreme conditions which the PCB and the printed legend are exposed to, and also overcomes the problem of settling of the pigment. The ink has the advantage of having a low viscosity at high temperatures and a high viscosity at room temperature, thus enabling good jetting from the print head (which requires low viscosity). The ink of the present invention meets the PCB legend ink test requirements of the ICP and displays excellent adhesion to the printed circuit board. The ink also exhibits resistance to various solvents that are part of the flux composition (e.g. iso-propyl alcohol), is very stable at high temperatures, and can withstand even dipping in a solder bath of 250-260°C.

These and other advantages of the present invention will become more apparent from the summary of the invention and detailed description of the invention that follow.

#### SUMMARY OF THE INVENTION

The present invention relates to an Ultra violet (UV) curable ink composition for printing a legend on printed circuit boards using an ink jet printer, comprising at least one reactive oligomer, a pigment, at least one reactive monomer, at least one photoinitiator, at least one additive, and at least one dispersing agent. The oligomers and monomers are selected in such a way, that the resulting inks, which are stable dispersions, prior to curing, have a high viscosity at room temperature (about 60- 200 centipoise), and low viscosity (about 10-20 cps) at higher temperature, which is set to be the jetting temperature (the temperature in which the printhead operates), between 50-80°C. Based on this property, the ink is heated when it comes into the printhead, thus enabling good jetting. This rheological profile prevents sedimentation of the pigments in the ink during storage, minimize surface defects of the printed legends due to pigment separation, and contributes to fixation of the ink droplet on the PCB during the printing process. The oligomer and monomer mixture are chosen in such a way that the rheological profile is obtained without the use of nonreactive diluents (solvents) leading to an ink that is close to 100% solids (preferably, above 90% solids,

“solids” referring to the material retained in the completely cured ink when exposed to temperatures of 100°C for 1 hour). This is advantageous in that this gives an increased coating thickness, thereby yielding a more opaque and resistant coating. In addition, the use of a high viscosity ink minimizes the need for reactive monomers, which are volatile and may pose certain health problems. The absence of volatile solvents also reduces the first drop or latency problem well known in inkjet applications where evaporation of solvents from the nozzles causes a local rise in viscosity leading to misplaced drops after a quiescent period. (Inkjet Technology and Product Development Strategies, Torrey Pines Research Publications, 2000).

According to preferred embodiments of the present invention the concentration of the oligomer and monomer are selected in order to achieve optimal overall viscosity and surface tension.

In addition the oligomers and monomers are chosen in such a way that they are able to withstand the extreme conditions required, particularly dipping in a solder bath at 260°C with no yellowing or damage to the print. Furthermore, the monomers are chosen so as to adhere and promote adhesion particularly to inert smooth surfaces such as exhibited by glossy soldermask found on the outer layer of some types of PCB.

Furthermore according to preferred embodiments of the present invention, the pigment has a particle size of less than 2 microns. This facilitates jetting without the ink clogging the printer nozzles. Preferably, the pigment has a particle size of less than 0.4 microns. The pigment may comprise organic or inorganic particles, depending on the required color.

Still further according to preferred embodiments of the present invention, the pigment is present in an amount of about 10-35% by weight of the ink composition. Preferably, the pigment comprises one or more metal oxides (for example, iron oxide particles, titanium dioxide particles, or titanium dioxide coated with functional groups) and the concentration of the pigment is selected in such a way which enables obtaining the required curing characteristics and also the proper hiding power and optical density. For example, if white legend ink is required, the preferred pigment is titanium dioxide, having a particle size in the range of 0.17-0.3 micrometer, and weight concentration of about 10-35%. In addition, in order to achieve the required optical density and hiding power, the ink may contain, in addition to the pigment,

functional fillers (often called "extenders"), such as fumed silica, clays and zeolites. Examples of such functional fillers are Aerosil 200, Aerosil 972, (Degussa), HDK H15P (Wacker HDK), CAB-O-SIL TS-350 (CABOT), ASP Ultrafine (Engelhard), Burgess 99, Burgess 10 (Burgess) and Zeolex 98 (Huber Eng. Materials). These materials often can lead also benefits in the rheological behavior of the ink.

The rheological behavior can be further modified by including rheological additives, for example, polyurea solutions capable of building a tri-dimensional net, such as BYK 410 (TM), BYK 411, polyhydroxycarboxylic acid amides, Byk 405, (from Byk Chemie), various micronized silicas such as Aerosils™, polyamide polymers Thixatrol (from Rheox) and others. An additional benefit of the rheological properties described above is the slowing down of the sedimentation of pigments during storage, which is a common problem in low viscosity paints containing titanium oxide pigments.

Moreover according to preferred embodiments of the present invention, the mixture of reactive oligomers and monomers is present in an amount from 60 to 90% by weight of the ink composition. Preferably, at least one of the monomers is an adhesion promoting monomer.

Additionally, according to preferred embodiments of the present invention, the ink comprises photoinitiator and a synergistic coinitiator. The coinitiator is chosen from the group comprising tertiary amines and acrylated amines.

Further according to preferred embodiments of the present invention, the ink also comprises at least one dispersing agent. Preferably, the dispersing agent is selected from the group consisting of dispersants with acidic groups, dispersants with amine groups, a high molecular weight anionic, cationic and nonionic polymer and polyacrylates containing pigment affinic groups.

Still further according to preferred embodiments of the present invention, the ink further comprises at least one wetting agent, preferably in the amount of about 0.01%-5% by weight of the ink composition.

The present invention also relates to a method for printing onto a printed circuit board comprising ink jet printing the UV curable ink composition as described above onto a printed circuit board.

The present invention further relates to a UV curable ink composition for printing on printed circuit boards using an ink jet printer comprising a trifunctional

urethane oligomer in an amount of about 10-30% by weight of the ink composition, a diacrylate monomer in an amount of about 5-15% by weight of the ink composition, an ethoxylated triacrylate monomer in an amount of about 10-20% by weight of the ink composition, an ethoxylated tetraacrylated monomer in an amount of about 5-15% by weight of the ink composition, an amine coinitiator in an amount of about 1-5% by weight of the ink composition, a photoinitiator in an amount of about 1-5% by weight of the ink composition and a titanium dioxide pigment in an amount of about 10-30% by weight of the ink composition.

Still further the present invention relates to a method for printing onto a printed circuit board comprising ink jet printing the heat curable ink composition described above onto a printed circuit board.

#### DETAILED DESCRIPTION OF THE INVENTION

The ink of the present invention comprises a mixture of oligomers and monomers which have 1 to 5 functional groups (which can undergo crosslinking by UV light), and are chosen to so as to optimize film properties after curing, such as hardness, flexibility, resistance to solvents and adhesion. The monomers serve as reactive diluents enabling a coating which is composed of close to 100% solids. Such monomers and oligomers can be selected from, but not limited to, epoxy acrylates, polyester acrylates, urethane acrylates, etc... For example, (from Sartomer) 1,6 hexanediol diacrylate (SR 238), aromatic epoxy acrylate (CN115), amine modified polyetheracrylate oligomer (CN 502), amine modified polyetheracrylate oligomer (CN550), acrylated amine (CN 386), aromatic monoacrylate oligomer (CN131), isobornyl acrylate (SR506), tris (2-hydroxy ethyl) isocyanurate triacrylate (SR368), dipentaerythritol pentaacrylate (SR399), Ethoxylated(4)pentaerythritoltetraacrylate (SR494), Ethoxylated3Trimethylolpropane Triacrylate (SR 454) and others. The mixture may be further comprised of monomers chosen to promote adhesion such as Tetrahydrofurfuryl acrylate (SR-285) and Tetrahydrofufuryl methacrylate (SR-203). In addition, since the PCB external layer is composed of a glass-epoxy layer, it is advantageous to use oligomers and monomers which have chemical moieties similar to the solder, such as epoxy groups.

The coating further comprises a mixture of photoinitiators designed to lead to a thorough cure of the film, both on the surface and in depth, by the choice of

photoinitiators for in depth and surface curing. Photoinitiators that function mainly for surface curing are such as benzophenone with ITX, Bis (2,4,6-trimethylbenzoyl)-phenylphosphineoxide(Irg819), together with Bis(2,6-dimethoxybenzoyl)-2,4,4-trimethyl-pentylphineoxide(Irg1800),2-Hydroxy-2-methyl-1-phenyl-propan-1-one(Irg1173), 2,4,6-Trimethylbenzoyl-diphenyl-phosphineoxyde (Darocure4265), through curing (such as Irgacure 819, 184 ), and also photoinitiators which are capable of being crosslinked together with the monomers and oligomers (such as amine acrylate). A further component of the photoreactive mixture is an amine coinitiator such as ethylene dimethyl amine benzoate (EDB) or an acryl amine. These synergysts serve as oxygen scavengers, sustaining the free radical reaction in the presence of oxygen. In addition, alkoxyated monomers and oligomers serve as efficient oxygen scavengers. This is critical in light of the sensitivity of the thin (5 to 20 micron) films deposited by the printer to oxygen quenching.

Another way to overcome the problem of oxygen scavenging, obvious to those well versed in the art of radiation cured films, is to use a cationic curing mechanism. Examples of coinitiators for the cationic initiated crosslinking are: triaryl sulphonium hexafluorophosphate CD1011, and diaryl iodonium hexafluoroantimonate (CD1012).

The pigment in the ink consists of organic or inorganic particles, depending on the required color. For example, white legend ink can be formulated with fine titanium oxide particles, as Kronos 2300 <sup>TM</sup>, Kemira 650, Tioxide TR92, Kemira L181, to mention just a few. Concentration of the pigment can vary, according to the required final optical density, or hiding power, and is typically between 10-35 %wt.

The particle size of the pigments should be below 2 um(micron), and more preferably below 0.4 um. It should be noted that the inclusion of the titania pigments in the ink present the problem of light reflection by the pigment particles, which may interfere with the curing process. For this reason, the photoinitiators and the pigments are carefully selected to allow proper curing and adhesion of the ink to the PCB.

In order to obtain a good dispersion of the pigment particles, dispersing agents such as Disperbyk 110, which is a copolymer with acidic groups, Disperbyk 168 which is a high molecular weight block copolymer with pigment affinic amine groups (from Byk Chemie), EFKA 1800, Texaphor 963, which is a polycarboxylic acid with amine derivatives (from Henkel) and others, may be used. More preferably, dispersion



agents which are capable of participating in the crosslinking reaction, such as LPN 7057, which is high molecular weight block copolymer in oligotriacrylate (from Byk Chemie), may be included in the formulation.

The ink may also contain wetting agents, such as Byk 333, Byk 307 which are polyether modified polydimethyl polysiloxane (from Byk Chemie), which help in obtaining smooth surfaces, and prevent surface problems such as dewetting, "fish eyes" etc.

To improve the quality of printed lines additives such as BYK 358, BYK 354 (polyacrylates from Byk Chemie), or other higher molecular weight additives may be added to improve adjacent drops coalescence, without decreasing surface tension.

## EXAMPLES

The examples provided are for the purposes of clarification and example only. They are in no way intended to limit the scope of the invention, as set out in the claims.

Example 1

Polyester/polyether based trifunctional urethane blended with hexandiol diacrylate (CN945B85)<sup>1</sup> 20% (percent by weight of the total ink composition)

1,6 Hexandiol Diacrylate 15% (SR238)<sup>1</sup>

Ethoxylated(4) pentaerythritol tetraacrylate 19% (SR 494)<sup>1</sup>

Tetrahydrofurfuryl Acrylate 10% (SR285)<sup>1</sup>

Ethoxylated3 Trimethylolpropane Triacrylate 9.5% (SR 454)<sup>1</sup>

Difunctional amine coinitiator (CN3861)<sup>1</sup> 2%

Bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide (Irgacure 819)<sup>2</sup> 1%

2-hydroxy-2-methyl-1-phenyl-propan-1-one (Darocur1173)<sup>2</sup> 2%

Titanium dioxide 20%

High weight molecular block copolymer with pigment affinic groups in oligotriacrylate diluent 1% (Byk-Lp N 7057)<sup>3</sup> 1%

Polyether modified poly-dimethyl-polysiloxane (Byk 333)<sup>3</sup> 0.5%

<sup>1</sup> Sartomer (Cray Valley)

<sup>2</sup> Ciba-Giegy

<sup>3</sup> Byk Chemie

The above ink composition provided good results after being jetted from an ink jet printer and cured at 700 mJ/cm<sup>2</sup>. The viscosity of the ink composition was 140cp at 25°C and 18 cp at 75°C (jetting temperature).

Example 2

Polyester/polyether based trifunctional urethane blended with hexandiol diacrylate (CN945B85) 20%

1,6 Hexandiol Diacrylate 15%

Ethoxylated(4) pentaerythritol tetraacrylate 19%

Tetrahydrofurfuryl Acrylate 10%

Ethoxylated(3 )Trimethylolpropane Triacrylate 9.5%

Difunctional amine coinitiator (CN386) 2%

1-hydroxycyclohexyl phenyl ketone (Irgacure 184) 4%

Ethyl-4-dimethylaminobenzoate (EDB) 3%

Fumed silica 1%

Polyether modified poly-dimethyl-polysiloxane (Byk 333) 0.5%

Modified polyacrylate with pigment affinic groups in triethylene glycol divinylether (Efka -4800)1%

Titanium dioxide 15%

## CLAIMS

1. An ultraviolet curable ink composition for printing on a printed circuit board using an inkjet printer comprising a mixture of reactive monomers and oligomers, at least one pigment, at least one photoinitiator, and at least one additive, wherein the mixture is formulated so that the ink has a high viscosity of about 40-200 cp at 25°C, and a low viscosity of about 10-20cp at a high temperatures of about 50-80°C, and wherein the cured image can withstand dipping in a solder bath at 260°C without substantial degradation.
2. An ink composition according to claim 1, wherein the ink contains over 90% solids.
3. An ink composition according to claim 1, wherein the pigment has a particle size of less than 2 micron.
4. An ink composition according to claim 1, wherein the pigment has a particle size of less than 0.4 micron.
5. An ink composition according to claim 1, wherein the pigment is present in an amount of about 10-35% by weight of the ink composition.
6. An ink composition according to claim 1 wherein the mixture of reactive oligomers and monomers is present in an amount from 60 to 90% by weight of the ink composition.
7. An ink according to claim 6, wherein at least one of the monomers is an adhesion promoting monomer.
8. An ink according to claim 1, wherein the ink comprises a photoinitiator and synergistic coinitiator, said coinitiator being chosen from the group comprising tertiary amines and acrylated amines.

9. An ink according to claim 1, wherein the ink includes a dispersing agent.
10. An ink according to claim 9, wherein said at least one dispersing agent is selected from the group consisting of dispersants with acidic groups, dispersants with amine groups, a high molecular weight anionic, cationic and nonionic polymer and polyacrylates containing pigment affinic groups.
11. An ink composition according to claim 1, wherein the pigment comprises one or more metal oxides.
12. An ink composition according to claim 11, wherein the pigment is selected from titanium dioxide or titanium dioxide coated with functional groups.
13. An ink composition according to claim 11, wherein the pigment comprises iron oxide particles.
14. An ink composition according to claim 1, wherein the additive comprises a functional filler aimed at achieving better hiding power and optical density.
15. An ink composition according to claim 14, wherein the said functional filler is selected from submicron silica, clays, zeolites, and mixtures thereof.
16. An ink composition according to claim 1, further comprising at least one wetting agent.
17. An ink composition according to claim 16, wherein the wetting agent is present in an amount of about 0.01-5% by weight of the ink composition.
18. An ink composition according to claim 1, wherein said at least one additive is a rheological additive.
19. An ink composition according to claim 18, wherein the rheological additive is selected from one or more of the group consisting of polyurea solutions,

polyhydroxycarboxylic acid amides, micronized silicas, and polyamine polymers.

20. A method for printing onto a printed circuit board comprising ink jet printing the UV curable ink composition of any one of the preceding claims onto said printed circuit board.

21. A UV curable ink composition for printing on printed circuit boards using an ink jet printer comprising a trifunctional urethane oligomer 10-30% by weight, a diacrylate monomer 5-15% by weight, an ethoxylated triacrylate monomer 10-20% by weight, an ethoxylated tetraacrylated monomer 5-15% by weight, an amine coinitiator 1-5% by weight, a photoinitiator 1-5% by weight and a titanium dioxide pigment 10-30% by weight.

22. A method for printing onto a printed circuit board comprising ink jet printing the heat curable ink composition of claim 21 onto said printed circuit board.